

Synthesis of High Magnetic Moment CoFe Nanoparticles via Interfacial Diffusion in Core/Shell Structured Co/Fe Nanoparticles

Chao Wang^{1,2,†}, Sheng Peng^{1,†}, Lise-Marie Lacroix¹, Shouheng Sun¹ (✉)

¹ Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

² Current Address: Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

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ABSTRACT

We report the synthesis of high magnetic moment CoFe nanoparticles via the diffusion of Co and Fe in core/shell structured Co/Fe nanoparticles. In an organic solution, Co nanoparticles were coated with a layer of Fe to form a Co/Fe core/shell structure. Further raising the solution temperature led to inter-diffusion of Co and Fe and formation of CoFe alloy nanoparticles. These nanoparticles have high saturation magnetization of up to 192 emu/g CoFe and can be further stabilized by thermal annealing at 600 °C.

KEYWORDS

CoFe nanoparticles, core/shell nanoparticles, magnetic nanoparticles, chemical synthesis

Introduction

High magnetic moment nanoparticles (NPs) are important for magnetic energy storage and magnetic data storage applications [1–4]. They are also superior contrast agents for highly sensitive magnetic resonance imaging (MRI) [5–10]. Body centered cubic (bcc) CoFe alloys have the highest saturation magnetization ($M_s = \sim 240$ emu/g) in this class of materials and are ideal magnetic materials for these applications. However, the chemical instability of nanostructured CoFe has made the synthesis of robust high magnetic moment CoFe NPs extremely challenging. Recent advances in NP syntheses have indicated that solution phase chemical synthesis is a reliable process for producing various monodisperse magnetic NPs by either simultaneous decomposition

of $\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\eta^4\text{-C}_8\text{H}_{12})$ (or $\text{Co}(\text{N}(\text{SiMe}_3)_2)_2$) and $\text{Fe}(\text{CO})_5$ [11], or co-reduction of $\text{Co}(\text{acac})_2$ and $\text{Fe}(\text{acac})_3$ (acac = acetylacetonate) [12]. However, CoFe NPs made by these processes are chemically unstable, being subject to fast oxidation into various oxides unless a chemically inert carbonaceous shell is coated under high-temperature reaction conditions [7]. It has been demonstrated that interfacial diffusion between the core and the shell in core/shell structured particles is a successful approach to various alloy NPs. For example, ferromagnetic FePt NPs were made by high-temperature reductive annealing of FePt/ Fe_3O_4 NPs [13], and AuAg alloy NPs were synthesized from Ag/Au core/shell NPs [14]. Therefore, starting from monodisperse Co NPs, one may be able to make core/shell structured Co/Fe NPs and convert these to CoFe NPs with better

Address correspondence to ssun@brown.edu

[†] These two authors made an equal contribution to the work.

control over size, stability, and magnetic properties.

Here we report the synthesis of CoFe NPs via interfacial diffusion between Co and Fe in core/shell structured Co/Fe NPs. Monodisperse Co NP seeds were first synthesized by thermal decomposition of cobalt carbonyl, $\text{Co}_2(\text{CO})_8$, and were then coated with Fe by thermal decomposition of iron pentacarbonyl, $\text{Fe}(\text{CO})_5$. CoFe alloy NPs were formed by heating the core/shell structured Co/Fe NPs at 250 °C under an Ar atmosphere. The as-synthesized CoFe alloy NPs had the bcc structure and saturation magnetization of 192 emu/g CoFe. After thermal annealing at 600 °C in Ar, the saturation magnetization of the NPs reached 230 emu/g, close to the bulk value (245 emu/g) of CoFe alloy. More importantly, when exposed to the ambient environment for 24 h, these CoFe NPs showed no obvious drop in saturation magnetization, indicating that the high magnetic moment alloy NPs are stable against oxidation and are suitable as building blocks for various high moment magnetic applications.

1. Experimental

All chemicals were used as received. $\text{Co}_2(\text{CO})_8$ and $\text{Fe}(\text{CO})_5$ were purchased from Strem Chemicals. Oleylamine (70%), dioctylamine (98%), oleic acid (90%), 1,2,3,4-tetrahydronaphthalene (tetralin, 99%), and octadecene (ODE, 90%) were from Sigma-Aldrich.

Synthesis of Co NPs. In a typical synthesis of 8 nm Co NPs, 0.3 mL of oleic acid, and 0.5 mL of dioctylamine were mixed and magnetically stirred in 20 mL of tetralin. The solution was heated at 100 °C for 1 h under a nitrogen flow to remove traces of moisture. After cooling down to room temperature, 0.54 g of $\text{Co}_2(\text{CO})_8$ was quickly added into the solution. The solution was then heated up to 100 °C for 30 min and subsequently to 210 °C for 20 min. After cooling down to room temperature, the Co NPs were precipitated by adding 20 mL of ethanol followed by centrifugation. The product was then dispersed in hexane and protected by argon.

Synthesis of CoFe alloy NPs. In a typical experiment, 20 mL of octadecene and 2 mL of oleylamine were mixed and magnetically stirred at

room temperature and then heated to 120 °C under an Ar atmosphere. After 30 min and under an Ar blanket atmosphere, 1 mmol of $\text{Fe}(\text{CO})_5$ was added to the solution followed by 59 mg of Co NP seeds in 2 mL of degassed hexane. The solution was kept at 120 °C for another 30 min, and then slowly (2–3 °C/min) heated to 180 °C and kept at this temperature for 30 min. The solution was further heated to 250 °C for 15 min. After cooling down to room temperature, the CoFe NPs were precipitated by adding 30 mL of isopropanol followed by centrifugation. The product was quickly dispersed in hexane and sealed under nitrogen for further applications.

In order to investigate the growth process, 0.2 mL aliquots of reaction solution were taken out by syringe after heating for 30 min at two different temperatures (120 °C and 180 °C), and quickly added to an excess of isopropanol to quench the reaction, and the resulting NPs were collected by centrifugation.

NP characterization. Samples for transmission electron microscopy (TEM) analysis were prepared by drying a dispersion of NPs on amorphous carbon-coated copper grids (Ted Pella). Particles were imaged using a Philips EM 420 transmission electron microscope (with an accelerating voltage of 120 kV). High-resolution TEM (HRTEM) images were recorded using a JEOL JEM-2010 microscope (with an accelerating voltage of 200 kV). X-ray diffraction (XRD) patterns of the particle assemblies were collected on a Bruker AXS D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Composition of alloy NPs was analyzed on a LEO 1560 scanning electron microscope (SEM) equipped with a spatially resolved energy dispersive X-ray spectroscopy (EDS) attachment. Magnetic studies were carried out using a Lakeshore 7404 high-sensitivity vibrating sample magnetometer (VSM) with magnetic field up to 1.5 T at room temperature. The wt% of metals in the NPs was obtained by measuring the weight difference before and after annealing the particles in a thermogravimetric analysis (TGA) pan at 800 °C under Ar for 1 h.

2. Results and discussion

Despite several recent reports [7, 11, 12], controlled alloying of Co and Fe in a single NP with tunable Co and Fe composition is still a challenging goal in synthesis. It is difficult to find Co and Fe precursors with chemical properties that have similar thermodynamics and growth kinetics under the same growth conditions. The rates of nucleation for Co and Fe are usually different, leading to limited control over the NP size and Co and Fe composition [15].

Previously, we have developed a synthetic scheme for AuAg alloy NPs involving annealing core/shell structured Ag/Au NPs [14]. Our further study indicated that such an interfacial elemental diffusion scheme could be readily applied to the synthesis of CoFe alloy NPs. This synthetic scheme is outlined in Fig. 1. In the synthesis, Co NP seeds are first coated with Fe by thermal decomposition of $\text{Fe}(\text{CO})_5$. Heating at a higher reaction temperature induces the elemental diffusion between Co and Fe at the core/shell structure, forming CoFe alloy NPs.

Co NP seeds were synthesized by thermal decomposition of $\text{Co}_2(\text{CO})_8$ in the presence of oleic acid and dioctylamine. After a rapid washing process and proper protection under argon atmosphere, the fresh Co NPs were added to an octadecene solution containing oleylamine and $\text{Fe}(\text{CO})_5$ [8]. The Fe-coating on the Co NPs was achieved by thermal decomposition of $\text{Fe}(\text{CO})_5$ at 180 °C. The Co/Fe NPs were then annealed in the same solution at 250 °C to form CoFe alloy NPs.

Figure 2 shows TEM images of the Co NP seeds and CoFe NPs synthesized in this work. Figure 2(a) shows the 8 nm Co NPs with a size deviation of less than 5%. The monodisperse Co NPs formed a hexagonal close-packed superlattice. Figures 2(b) and 2(c) are images of the CoFe NPs obtained by coating the Co seeds (Fig. 2(a)) followed by thermal annealing at 250 °C. The NP size was increased from 8 nm to 11 nm due to addition of Fe. The atomic ratio of Co to Fe in the final product was measured to be 0.55 by EDS (Fig. S-1 in the Electronic Supplementary Material). Figure 2(d) shows the HRTEM image of a single CoFe NP. The inter-fringe distance was measured to

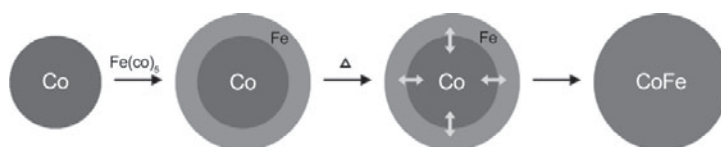


Figure 1 Schematic illustration of CoFe alloy NP synthesis by interfacial diffusion of Co and Fe in the core/shell structure Co/Fe NPs

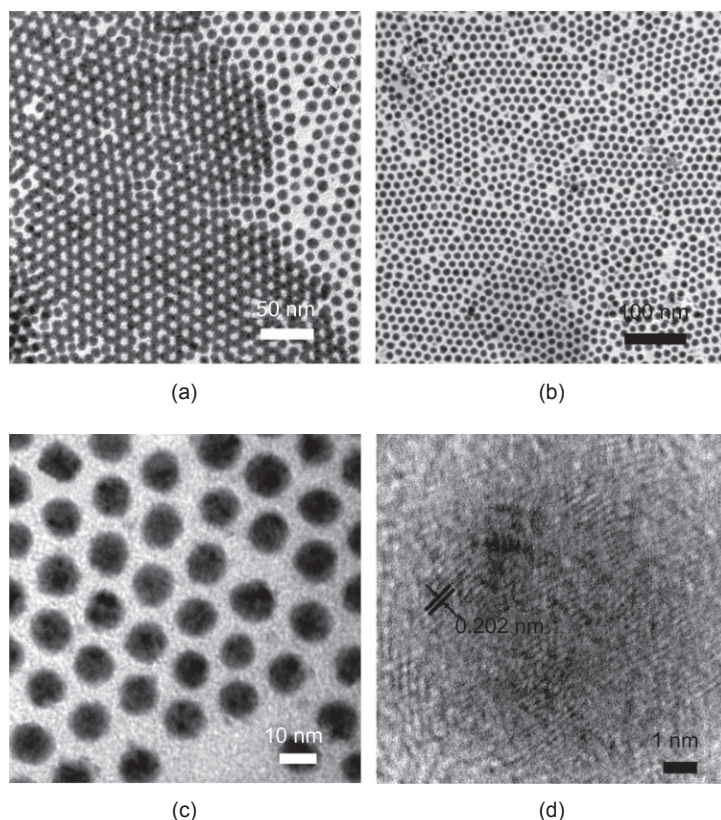


Figure 2 TEM images of (a) 8 nm Co seeds; (b) and (c) 11 nm CoFe NPs; (d) HRTEM image of a single CoFe NP

be 0.202 nm, corresponding to (110) planes of the bcc phase of CoFe. The HRTEM image also shows that the NP had a polycrystalline structure.

In order to investigate the growth mechanism, the NPs were collected and analyzed at various stages of the growth. Figure 3 shows TEM images of the NPs obtained at 120 °C and 180 °C. It can be seen that at 120 °C, a 1–2 nm thick shell (gray) formed on some Co particles (dark). The gray shell is iron oxide coming from the facile oxidation of Fe when the NPs were exposed to air. The iron oxide shell has a much lower electron density than the metallic Co core and therefore looks much lighter. The TEM images also show some separate light species of

irregular shapes with sizes of 5–10 nm in the sample collected at 120 °C. These are likely to be iron oxide NPs formed by separate Fe nucleation/growth in the reaction solution, implying incomplete consumption of $\text{Fe}(\text{CO})_5$ at this stage. However, the NPs collected at 180 °C had a much more uniform core/shell structure, with a shell thickness of ~2 nm. No free iron species can be seen at this stage. Upon further heating of the core/shell Co/Fe at 250 °C, the Fe (oxidized to iron oxide) shell is difficult to see in the TEM image and the NP size becomes 11 nm (Fig. 2), which indicates the diffusion of Fe into the Co core and the formation of CoFe alloy NPs. It should be noted that the diffusion of Fe into the Co core may start during the coating process. This diffusion may have a minimal effect on alloy formation due to the

low coating temperatures and slow diffusion rate, however [14].

Figure 4 shows the XRD patterns of the as-synthesized CoFe NPs and after annealing at 600 °C for 1 h (in Ar). The pattern after annealing corresponds to bcc CoFe. The peaks of the as-synthesized NPs are very broad because of the polycrystalline nature of these NPs, as observed in the HRTEM image (Fig. 1(d)). The broad peak around 25° is due to the presence of carbonaceous ligands on the particle surface. After annealing, the diffraction peaks become stronger and sharper, indicating enhanced crystallization of the NPs.

Magnetic properties of the CoFe NPs were studied by VSM. The as-synthesized NPs are superparamagnetic with saturation magnetization

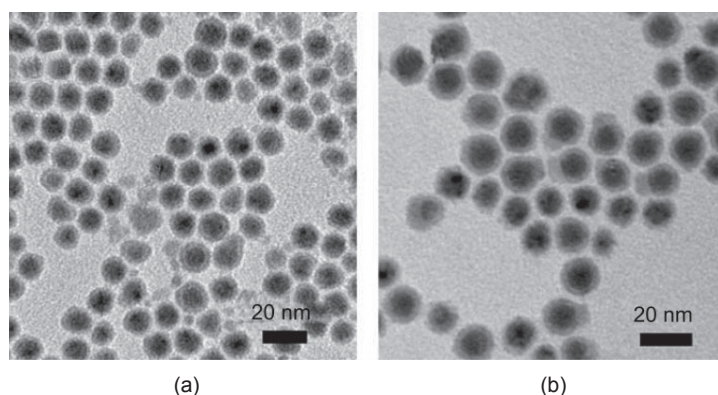


Figure 3 TEM images of the NPs collected at (a) 120 °C and (b) 180 °C

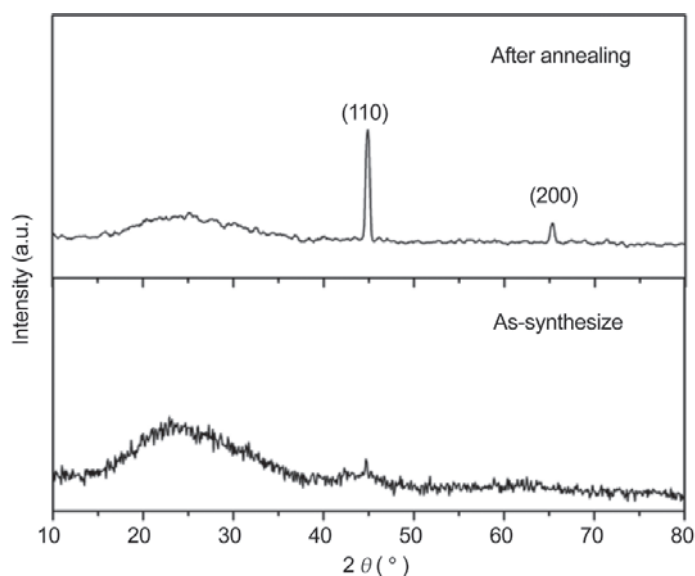


Figure 4 XRD patterns of as-synthesized CoFe NPs and after annealing at 600 °C for 1 h



(M_s) up to 95 emu/g NPs. This corresponds to 192 emu/g CoFe metal (Fig. 5(a)), considering that 50.5% by weight of the NPs was contributed by organic species (see Experimental section). The amount of organic species is rather high, due to the rapid washing process which leaves organic residues in the product. A saturation magnetization of 192 emu/g is $\sim 22\%$ lower than the bulk value of CoFe alloy (245 emu/g) and the difference is likely caused by the polycrystalline nature of these NPs and by NP surface oxidation. After annealing in Ar (600 °C, 1 h) the saturation magnetization is increased to 230 emu/g CoFe, probably owing to the increase in crystal grain size after annealing.

The as-synthesized NPs are not stable when exposed to air. Figure 5(b) shows the change of M_s for the as-synthesized CoFe NPs with air-exposure time. The value of M_s for the as-synthesized NPs (192 emu/g CoFe) was reduced to ~ 140 emu/g after exposure for an hour due to the surface oxidation. At longer exposure times, the value of M_s reached a constant value of ~ 120 emu/g, suggesting that the formed thicker oxide layer resulted in much slow oxidation of the CoFe NPs. The chemical stability of the NPs was improved by high temperature thermal annealing. As indicated in Fig. 5(a), the annealed CoFe NPs showed a very small drop (~ 10 emu/g CoFe) in magnetization after exposure to air for 24 h. One possible reason for this enhanced chemical and

magnetic stability is the formation of a carbonaceous coating from the organic surfactants around CoFe NPs during the high-temperature annealing process [7]. It can also be due to the crystallization of the surface oxides (formed when exposed to air) under annealing; a similar observation has been reported in the synthesis and stabilization of Fe NPs [8].

3. Conclusions

The paper reports a new synthesis of high magnetic moment CoFe NPs in an organic solution phase from core/shell structured Co/Fe NPs via the interfacial diffusion of Co and Fe in the core/shell structure at 250 °C. The unique feature of this synthesis is that it uses monodisperse Co NPs as seeds and by controlling the Fe coating, monodisperse Co/Fe NPs and therefore CoFe NPs can be readily produced. The as-synthesized CoFe NPs are polycrystalline with saturation magnetization reaching 192 emu/g CoFe metal and are not air-stable unless they are annealed at 600 °C. These high magnetic moment NPs may serve as building blocks for fabricating nanocomposite magnets with maximum energy product or for other nanomagnetic applications.

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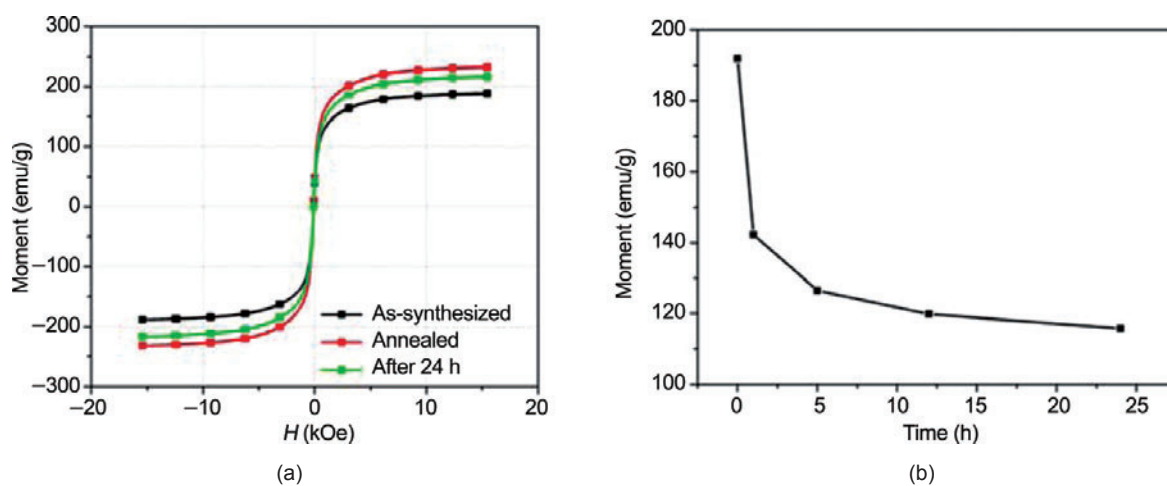


Figure 5 (a) Hysteresis loops of the as-synthesized (black) and the annealed (red) CoFe NPs, and the annealed (600 °C in Ar for 1 h) NPs after 24 h of exposure in air (green); (b) dependence of saturation magnetization (M_s , emu/g CoFe) of the NPs on time exposed to air in hexane dispersion

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